CHAPTER 1

INTRODUCTION

1.1 Atomic Spectrometric Techniques for Elemental Analysis

Atomic spectrometric techniques have been employed for elemental analysis since the early part of this century (Herzberg, 1944). These techniques are based on the electronic transitions in the atoms of the elements which result in the emission of characteristic spectral lines. The wavelengths of the spectral lines enable one to identify elements present in a sample (qualitative analysis), whereas the spectral intensities determine the concentration of those elements (quantitative analysis).

The atomic spectrometric techniques can be divided into three main groups, i.e., atomic emission, atomic absorption and flourescence depending on the electronic transition process observed. Table 1.1 gives a list of these techniques, the different modes of atomisation involved and their applicability for the analysis of solids, liquids or solutions.

Among the various atomic spectrometric techniques, arc/spark AES, XRF and glow discharge sources are the only ones suitable for direct solids analysis. There have been continuous interest in the development of direct solids analysis in an attempt to alleviate tedious sample dissolution and digestion procedures which are essential to most solution techniques. The arc/spark atomic emission spectrometry has consolidated its role in metals and alloys analysis as the most common analytical tool for process and product quality control for the metals industry. The advent of reproducible and stable discharge source as well as recent

Class	Techniques	Solid	Liquid	Solution
Atomic Emission	Arc/Spark Atomic EmissionSpectrometry (Arc/Spark AES)	Y	Y	-
	Flame Atomic Emission Spectrometry (FAES)	-	Y	Y
	Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)	(Y)	Y	Y
	Direct Current Plasma-Atomic Emission Spectrometry (DCP-AES)	-	Y	Y
	Microwave Induced Plasma-Atomic Emission Spectrometry (MIP-AES)	-	Y	Y
	Glow Discharge Atomic Emission Spectrometry (GDAES)	Y	-	(Y)
Atomic Absorption	Flame Atomic Absorption Spectrometry (FAAS)	-	Y	Y
	Graphite Furnace Atomic Absorption Spectrometry (GFAAS)	(Y)	-	(Y)
	Glow Discharge Atomic Absorption Spectrometry (GDAAS)	Y	-	-
Atomic Fluorescence	Flame Atomic Fluorescence Spectrometry (FAFS)	-	Y	Y
	Glow Discharge Atomic Fluorescence Spectrometry (GDAFS)	Y	-	-
	X-ray fluorescence (XRF)	Y	-	-

Y-Yes
(Y)-Yes but by special techniques

Table 1.1 Atomic spectroscopic techniques and their suitability for solid, liquid or solution analysis.

progress in computer and software for data acquisition and analysis contributed to the maturation of this technique for the metal industry satisfying the need in speed, precision and accuracy and sufficient sensitivity. On the other hand, development is also seen in XRF which has found wide spread applications in geological analysis and analysis of light alloys.

Glow discharge is a versatile atomisation source which has been utilized in atomic absorption, atomic emission, atomic fluorescence spectrometry or as an ion source in atomic mass spectrometry. It is gaining popularity in recent years and some important applications in the analysis of metals and alloys have been reported (Gough, 1976 & 1989; McDonald, 1977; Kruger *et al.* 1977; Fujita *et al.*, 1981; Broekaert, 1987; Harrison *et al.*, 1988 & 1990; Marcus *et al.*, 1994). There has also been increasing research on the application of glow discharge for the analysis of nonconducting powder or solution residue samples (El Alfy *et al.*, 1973; Brenner *et al.*, 1987; Winchester and Marcus, 1988; Ehrlich *et al.*, 1991; Chakrabarti *et al.*, 1990 & 1991; Tong and Harrison, 1993).

1.2 Objectives and Scope of the Present Study

The main objective of the present study is to investigate the optimum conditions for the direct analysis of non-conducting powder samples using glow discharge atomic emission spectrometric (GDAES) technique. The study involves the following aspects: (i) construction of a glow discharge source for compacted solid cathode; (ii) application of the photodiode array detector for the atomic emission spectral measurements; (iii) characterisation and evaluation of suitable compacting materials for GDAES, in particular with respect to the effects

of reactive species and residual gases in the discharge; and (iv) evaluation of GDAES for compacted model oxide compounds and geological samples analysis.

1.3 Basic Features of Gas Discharges

The term "gas discharge" refers to the phenomenon of a flow of electric current through a gaseous medium. This requires that a fraction of the gas particles is ionized and that an electric field exist to accelerate the charged particles to form a current. All gas discharges are in their steady state, in contrast to the transient discharge such as the spark discharge and they may be classified generally according to the current they carry. Depicted in Fig. 1.1 is the characteristic current (A) and voltage (V) curve of a gas discharge. The three major types of gas discharge are : (i) the Townsend discharge (ii) the glow discharge and (iii) the arc discharge. Most often, these discharges are excited by a d.c. power sources and take place between 2 electrodes.

The Townsend discharge is a non-luminous discharge. It is characterized by a very small current, from the range of nano- to micro- amperes. It is not a self sustaining discharge since it does not entirely produce its own ionization, but requires external source or agents, e.g. x-rays or uv lights to produce electrons either in the gas or at a negatively biased electrode.

The arc discharge, in contrast to the Townsend discharge, is an intense luminous discharge. It operates at high current (in the region of 0.1 to a few amperes). The thermionic electron emission from the cathode is known to be the source of electrons in the discharge. The arc discharge, from which severe erosion

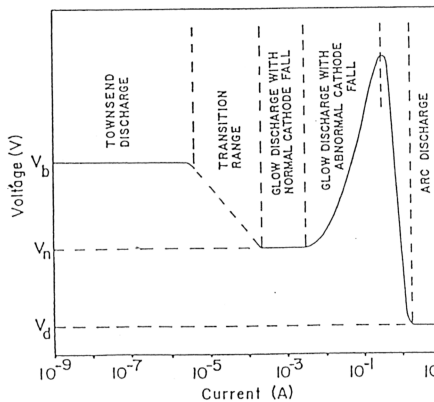


Figure 1.1 Schematic representation of current-voltage characteristics of gas discharges.
(From Loeb, 1939)

may result, has found employment as an excitation source for analytical spectrographic emission (Barnes., 1976 ; Boumans, 1966).

The glow discharge is a luminous discharge and it operates at current from a few mA to a few hundreds mA. Glow discharge is the generic name for an extensive class of phenomena associated with full conduction processes through a low pressure gas. It can be conveniently described as a discharge in which the cathode bombarded by particles and light quanta from the discharge gas emits electrons (Boumans, 1972). Thermal effects are either absent or at least not a necessary condition for maintaining the discharge. The glow discharge may be excited by a dc source or rf (radio frequency) source. The dc glow discharge at low pressure of about 10 Torr is probably the most commonly recognised form of gas discharge.

1.4 The Characteristics of the dc Glow Discharge

The glow discharge is one form of plasma, a partially ionized gas consisting of approximately equal concentrations of positive and negative charges plus large numbers of neutral species. The glow discharge may be excited by a dc source or by an rf source.

In general, the conventional dc glow discharge is established by applying a potential of about 500 to 1000 V or higher between two planar electrodes in a vacuum chamber which is filled with an inert gas at 1 to 10 Torr pressure. The filler gas normally used for most GD devices which is employed for chemical analysis purposes is argon. The glow discharge is characterized by up to eight distinct zones or regions, depending on the configuration of the discharge,

which develop between the electrodes. Figure 1.2 shows the various discharge zones which are observed in a conventional dc glow discharge. It is due to these zones that the glow discharge normally manifests a stratification into dark and bright luminous layers. The radiative relaxation of electronically excited species is responsible for the luminosity of various regions of the discharge. Dark spaces correspond to those regions where excitation cross section is small, thus minimizing any electronic excitation and subsequent radiative relaxation. Generally, analytical applications of the glow discharges utilize the primary luminous region of the negative glow. Such discharges are operated under conditions that limit the number of dark and luminous regions that extend from the Aston dark space to the Faraday dark space.

Since the glow discharge is a self sustaining discharge, the electrons required to maintain the discharge are produced from the cathode surface due to the bombardment of the cathode by positive ions. The bombarding positive ion species is thought to become neutralized by a field emitted electron just before impact with cathode surface (G.K. Wehner, 1975). The neutralization energy is transferred in an Auger-type transition to the lattice electrons which may cause the ejection of secondary electrons from the cathode surface. The secondary electrons form a negative space charge in a region called the ***Aston dark space*** which is directly adjacent to the cathode surface. These electrons are ejected from the cathode at energies less than 1 eV. The Aston dark space is therefore characterized by the presence of electrons of low energy originating from the cathode (i.e electrons having energies less than threshold excitation energies) which is not sufficient for

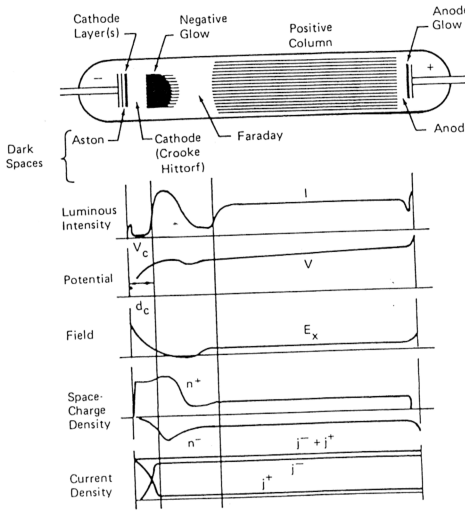


Figure 1.2 Discharge zones of a conventional dc glow discharge. (From Nasser, 1971)

exciting an atom. Hence the Aston dark space is seen as a dark narrow band. The current in this region is mainly carried by positive ions heading towards the cathode.

Next to the Aston dark space is the weakly luminous cathode layer. In this region the electric field become weaker, and the electron in this layer is a more efficient excitation and ionization agent, causing electron multiplication and ionization of the discharge gas.

Still further away from the cathode, is the ***cathode dark space.*** A thin layer which exhibits a high positive-ion density and shows relatively little optical emission. The electric field in this region becomes even weaker so that those fast electrons that have not lost their energy through inelastic collisions are able to ionize in this layer. Between the cathode and the negative glow boundary, the number of electrons able to cause ionization has increased through multiplication, thus resulting in the creation of a large number of positive ions simultaneously. A large net positive space charge is established throughout the cathode dark space. This positive space charge produces a large potential gradient and most of the discharge voltage is taken up here. The voltage across the cathode region from the cathode to the anode end of the cathode dark space is known as the cathode fall potential. Approaching the negative glow from the cathode dark space, electron multiplication takes place, diminishing the positive space charge. By the end of the cathode dark space, the current is nearly all carried by the electrons, present in great numbers.

The ***negative glow*** region, which fills much of the volume in small analytical sources is the region found next to the cathode dark space. It is a region

of intense radiation. Two main groups of electrons enter this region from the cathode dark space: fast electrons, produced near the cathode, which have not suffered inelastic collisions in the cathode dark space and; slow electrons, those created in the cathode dark space which are less energetic as a result of undergoing inelatic collisions. The greater part of the current in this region is carried by these electrons, many of which have sufficient energy to create sustaining ionization and to excite discharge gas atoms to emit the characteristic glow. The maximum brightness of the discharge occurs a short distance away from the leading edge (cathode side) of the negative glow, where energy-depleting collisions give rise to electrons having energies at which large inelastic collision cross section are observed.

A small number of electrons which further penetrate into the negative glow, produce both ionization and excitation. However they lose their energy gradually with distance. As the electrons are slowed down, the negative space charge reaches a maximum, and the energy available for excitation and ionization is exhausted. It is at this point that the ***Faraday dark space*** begins. The Faraday dark space is characterized by the presence of ground state particles and low energy electrons. In the Faraday dark space, the field again increases withdrawing electrons from the fringe of the negative glow. The accelerated electrons acquire enough energy to cause excitation and ionization in the next zone, called the ***postive column***. The positive column is a luminous zone and easily mold itself to the shape of the tube containing it.

An increase in pressure results in the compression of the cathode dark space, negative glow and Faraday dark space which contract toward the

cathode. A decrease of pressure produces a reverse effect, and if the voltage is not increased, the discharge goes out. (Nasser, 1971).

Normal and Abnormal Glow Discharge

The glow discharge can be operated in the normal or abnormal mode. The difference is readily distinguished from the Figure 1.1. When a discharge is operated under conditions such that the voltage remains constant as the current is increased by several order of magnitude (e.g., from 10^{-4} to 10^{-2} A), the discharge is said to be a normal glow discharge. This is because the glow area does not completely cover the cathode surface. Under this conditions, the current density at the cathode and the discharge voltage remain constant, while the area of the cathode covered by the glow expands proportionally with the current. When the cathode is fully covered, an increase in current is necessarily associated with a rise of the current density. This increase in the current also requires a higher voltage for driving the discharge, since the current density must now increase. The region with the positive characteristic is that of the abnormal glow discharge. It ends where thermal emission of electrons from the cathode begins and the discharge as shown in Figure 1.1 is an arc discharge. From an analytical standpoint, it is advantageous to operate a glow discharge in the abnormal mode, as this provides a homogenous sampling of the entire cathode surface area.

A special type of glow discharge configuration which has been employed in this study as an analytical source is the Grimm glow discharge lamp which is illustrated in Figure 1.3. The Grimm discharge is an obstructed discharge where no discharge can develop between the space of the anode and the cathode

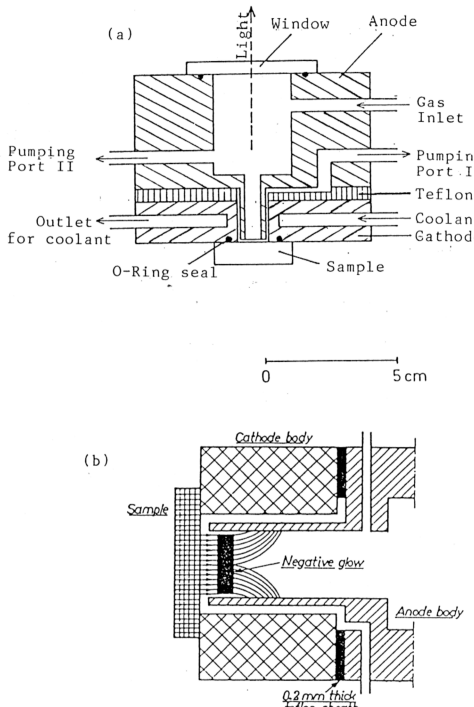


Figure 1.3 (a) Grimm (planar cathode) glow discharge source.
(b) Schematic diagram illustrating the type of obstructed discharge that ensues in the Grimm glow discharge source.

(a)- From Grimm, 1967
(b)- From Boumans, 1972

that immediately faces one another. Instead a steady discharge ensues between the inner wall of the anode and the part of the cathode located opposite the cylindrical anode cavity. The discharge volume and sputtering area on the cathode are effectively limited to the region enclosed by the anode. This is because the cylindrical anode is positioned within a single cathode dark space length from the cathode. The luminuous part of the discharge consist chiefly of the negative glow. The luminous zone is separated from the inner anode wall by an annular anode dark space. The Grimm discharge source has found its application in the area of solids atomic emission spectrometry since the negative glow produced in this configuration is intense.

The sputtering process that occur at the surface of the cathode and the excitation/ionization processes that occur in the negative glow are discussed in the following section.

1.5 Atomization by Cathodic Sputtering in the Glow Discharge.

Cathodic sputtering is the inherent phenomenon in the operation of a glow discharge that makes it useful in analytical spectrometry. It provides a means of obtaining directly from the sample an atomic population which is subsequently subjected to direct excitation and ionization. Discharge gas ions formed at the cathode dark space and negative glow interface are accelerated to the cathode surface, where upon collision an assortment of secondary particles is released, including the electrons to help sustain the discharge. Figure 1.4 gives a representation of sputtering, excitation and ionization processes in the glow discharge. Ferreira and Human (1981) demonstrated that the greater part of the

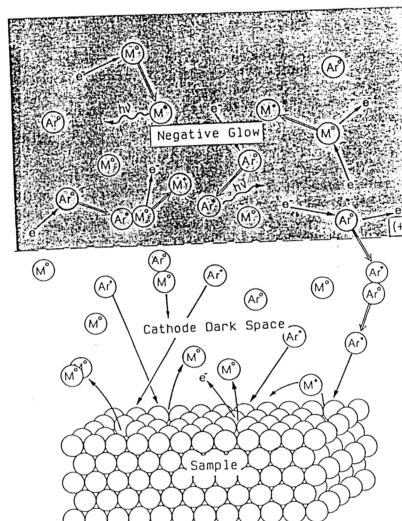


Figure 1.4 Illustration of cathodic sputtering in an abnormal glow discharge. (From Harrison and Bentz, 1988)

sputtered analyte in a conventional glow discharge source is present as ground-state neutral atoms.

The effectiveness of the sputtering process in releasing atoms from the solid state is measured by the value of the sputtering yield, (Y) (Boumans, 1972). It refers to the number of atoms removed from the surface as a result of the impact of one primary ion. Figure 1.5 shows the sputtering yields of a wide range of elements sputtered by argon ions at 44 eV. The sputtering yields of most elements vary within a narrow range of 0.5 to 1.8.

In the analysis of a multicomponent system, the effect of the difference in the sputtering yield of various elements in the sample is of great concern. The difference in the sputtering yield will affect the atom population of the various elements in the plasma as the sampling integrity is affected. It is essential that the elemental composition of this atom population accurately reflect the elemental composition of the sample. Glow discharge passively correct for preferential sputtering to maintain sampling integrity. The initial atom population shows concentration values that are artificially high for elements having a large sputtering yield. This will result in the enrichment of the surface with elements having smaller sputter yield leading to the eventual attainment of an equilibrium situation. From the point in time when this equilibrium is established, the sputtering rate is controlled by that element having the smallest sputtering yield. After some initial time period during which equilibrium is attained, the population of the atomic vapor approximates the population of the solid sample (Coburn, 1976).

The conditions placed by trace element method on the glow discharge sampling mode are: (i) representative atomic populations be created from

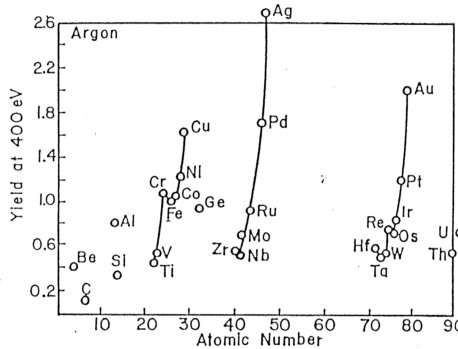


Figure 1.5 Neutral atom sputter yields for various elements. (From Carter and Colligon, 1968)

elemental concentrations that range over many orders of magnitude, and (ii) the plasma populations should remain stable with respect to analytes of different sputtering yield throughout the measurement process (Harrison, 1992).

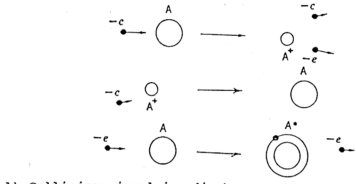
1.6 Excitation and Ionization Processes in the Glow Discharge

Besides atomising the analytical sample, the glow discharge excites and ionizes sputtered sample atoms through various energy transfer processes. The excitation and ionization in glow discharges are mainly due to electron impact (collision), but other processes also contribute (Flügge, 1956). Collisions in the negative glow result in electronic excitation of sputtered and discharge gas species. Energy (in the form of kinetic or potential energy) transfer from a collision partner excites electrons of the target species to higher energy states, or in some instances removes an electron completely. Such processes are not only crucial to the maintainance of a stable discharge, but they are also the nuclear to the analytical utility and plasma chemistry of the discharge.

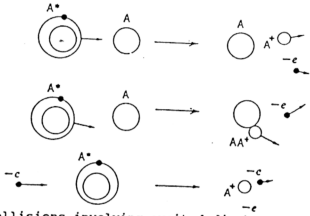
The three principal types of collisions involving argon gas discharge in the negative glow: (a) collisions involving discharge electrons, (b) collisions involving excited discharge species, and (c) collisions involving discharge ions are illustrated in Figure 1.6 (Nasser, 1971).

1.7 Glow Discharge Analytical Atomic Spectrometry

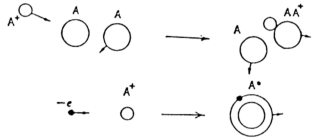
Figure 1.7 illustrates graphically the various analytical methods that employ a glow discharge. As the discharge ablates the cathodic (sample) material



1) Collisions involving discharge electrons



2) Collisions involving excited discharge species



3) Collisions involving discharge ions

Figure 1.6 Typical collisional processes occuring in the negative glow. (From Nasser, 1971)

into the plasma, elemental species are available for a number of different analytical measurements.

The large atomic population in the discharge makes sensitive atomic absorption (AA) measurements possible. A fraction of these atoms which is excited undergo subsequent decay to give atomic emission (AE). Furthermore, atoms may be stimulated by external light sources for atomic flourescence (AF). Some atoms may undergo ionization through the lost of one electron by collision to give ions which could be sampled by mass spectrometry. Because of the ready compatibility between the GD source and mass spectrometry, GD-mass spectrometry (GDMS) is currently the most prominent analytical techniques among the GD-based spectrometries for elemental analysis. With GDMS, metals and nonmetals can be detected rapidly and routinely in solids at part-per-billion levels with minimal matrix effect (Jakubowski *et al.*, 1988; Jakubowski *et al.*, 1991*)*. Akin to the ICP-MS technique, multielement isotopic information can be acquired, and ion intensities are linear from trace to major levels.

1.7.1 Glow Discharge Atomic Emission Spectrometry

In glow discharge, the sample material volatilization (atomization) is solely based on cathodic sputtering, which excludes selective volatilization (atomization) and related interferences (which are commonly found in the arc and spark sources). However, it is possible to adjust the cathode temperature carefully by regulations of the discharge current and/or external heating to allow for the selective volatilization (atomization) of elements or species from a complex matrix,

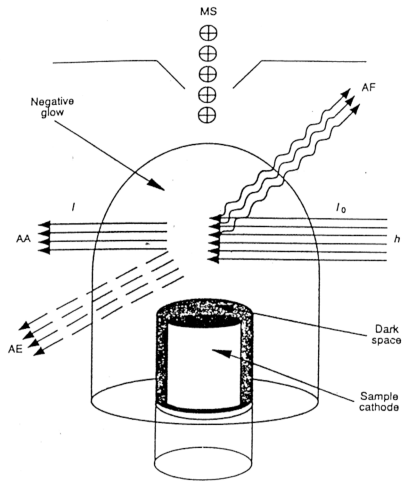


Figure 1.7 Analytical methods using glow discharges. (From Harrison *et al.*, 1990)

especially when selective removal of sample constituents is needed (Broekaert, 1987).

Owing to the non-local thermal equilibrium (LTE) character of the glow discharge, high spectral line to background intensity ratios are obtained for the analyte elements. The spectra hence consist mainly of the most sensitive lines, which are narrow because of the low Doppler and pressure broadening.

The common GD configurations for atomic emission spectrometry include hollow cathode lamps and Grimm or obstructed glow discharge lamp (Grimm, 1968) which uses flat solid sample as cathode. These GD configurations are powered by direct current while in more recent development of GDAES technique, the coupling of radio frequency power to GDAES sources for direct analyis of nonconducting samples (eg. glass, ceramics, soil etc.) is being explored.

Hollow Cathode Discharge (HCD)

Hollow cathode discharge has long played the essential role as spectral line source for atomic absorption spectrometry. A typical HCD source consisting of a cavity cathode is shown in Figure 1.8. The hollow-cathode effect can be visualised as a glow with two parallel cathode plates being brought sufficiently close (about 8 mm or less) to each other until the two cathode glow regions overlap and begin to coalese (Figure 1.9). As a result of this coalescence, the current density in a hollow cathode can be several orders of magnitude larger than that obtained using a single planar cathode at the same cathode fall of a conventional glow discharge (Little and von Engel, 1954). The dramatic increase in the intensity of radiation emitted from the negative glow observed leads to the

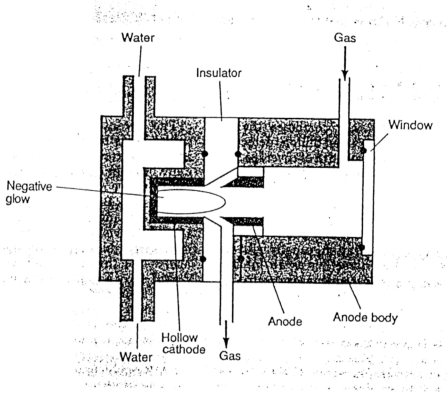


Figure 1.8 The hollow-cathode discharge. (From Harrison *et al.*, 1990)

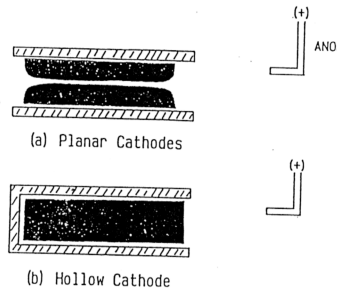


Figure 1.9 Hollow cathode discharge phenomenon. (a) two negative glows from planar cathodes are brought together to then achieve a coalescence as shown in (b) a typical hollow cathode discharge. (From Harrison and Bentz, 1988)

usefulness of this device as an optical emission source. For a given voltage applied on the hollow cathode, the plasma is concentrated within the constraining cavity, which resulted in enhancement of analytes emission intensities. The HCD source is characterised by its high stability, reproducibility of intensity measurements, the sharp profile of emitted spectral lines, reduced self-absorption phenomena, negligible background interference and low matrix effects (Caroli *et al.,* 1982). It has been shown by Mandelstam and Nedler (1961) that the analytes has a very long residence time in the excitation zones which results from the cathode geometries of the HCD source which leads to very low detection limits (microgram per gram). This is further strengthened by the departures of the hollow cathode discharge from local thermal equilibrium (LTE). Because of this the hollow cathode discharge display increase in line to background ratios when compared to those of LTE sources (Falk, 1977).

Typical operating conditions for the hollow cathode discharge lamp are 200-500 V, 5-100 mA, and 0.1-1.0 Torr. In hollow cathodes, the samples is placed as a disk at the base of the holow cathode or a hollow cathode is machined from the sample. Atomization takes place by cathodic sputtering alone and no equilibrium in sample ablation is attained, which is in contrast to a conventional GD source. Similar to the flat cathode technique, this technique can be used for the analysis of metals and electrically non-conducting powders (must be made to conduct by pulverizing and mixing with a conducting matrix). For analyses of metals and alloys, the hollow cathode is machined from the bulk metal. Detection limits in the range of 0.1 to 1.0 ppm levels ($\mu g\ g^{-1}$) can be achieved (Harrison *et al.,* 1990). Microanalyses with liquid sample aliquots can be performed by

transferring them into metal or graphite cathodes and exciting the dry solution residues (Harrison and Prakash, 1970a).

Harrison and Prakash (1970b) conducted trace element analysis (Pb, Cu, B and Sn) of solution residues by hollow cathode excitation (demountable hollow cathodes used are of stainless steel, for strongly acidic solution of Pb, Cu and B and graphite for Sn). The elements determined, the ranges (ppm) at which rectilinear response is seen for these elements, the emission lines used and the filler gas are reported as follows: Pb (0.2 to 1.2, 405.78 nm, Ar), Cu (0.1 to 0.8, 324.75 nm, He), B (0.1 to 0.5, 249.70 nm, Ar), Sn (0 to 5, 326.23 nm, Ar). The method is accurate to within ± 3 % to 5 %.

Caroli *et al.* (1977; 1978; 1979; 1980) conducted comparative studies on the analytical performance of the HCD, glow discharge and the spark emission sources. Samples used in these studies include brass, copper, aluminium and steel. Two types of discharge gases were used, Ar and He. Ar is shown to have advantages over He. In these studies they concluded that HCD give better stability, reprodubility, precisions and stable excitation.

Caroli *et al.* (1983) used a HCD for the determination of trace elements (Ag, Al, Cr, Mn, Ni, Pb, Sn, Ti and Zn) in mineral ash residues from the ashing of biological material. The method uses samples previously diluted with a 1:4 graphite-copper powder mixture to render them electrically conductive and subsequently pressed into the form of hollow cylinders. They reported linearity of calibration plots extending over at least two order of magnitude and the use of an internal standard (Ga) greatly improved the linearity than plotting emission intensities only. The detection limits reported were said to be satisfactory (0.1 μg g^{-}

^{1} for Cr to 5 μg g^{-1} for Pb). In another study on biological materials, Caroli *et al.* (1983) determined Al, As, Ca, Cu, Ga and Zn in the presence of simple synthetic liquid matrices of H_3PO_4, $NaNO_3$ or $NaNO_3$-KNO_3 and in liquid samples from the mineralization of biological materials over a wide range of concentration and internal ratios. This was conducted to study the matrix effect on analytical signals. The HCD analysis was done on solution residues of the matrices and biological liquid samples. The results were compared with those obtained by a.a.s. and a.e.s.; the hollow-cathode discharge emission source is less subjected to matrix effects than the other methods.

Caroli *et al.* (1984), investigated the detection limits of the HCD source in atomic spectroscopy for various types of samples (solution dry residues, pelleted powders and electrically conducting materials. The effects of the specimen's physical state as well as of the simultaneous presence of the other analytes are also elucidated. Their experimental data supported the view that the mentioned effects are almost negligible. Detection limits were reported for Ag, Al, As, Bi, Cd, Cr, Cu, Fe, Ga, Mn, NI, Pb, Se, Sn, Te, Ti and Zn. Detection limits for solution residues and conducting solids ranges from 0.06 ppm for Al to 3 ppm for Pb whereas detection limits for pelleted powder ranges from 1 ppm for Sn to 10 ppm for Cr. They concluded that the detection limits obtained with the HCD agree within one order of magnitude. The high values in detection limits for the pelleted powder was explained by the smaller surface of the pellet being subjected to the discharge.

Ryu *et al.*, 1987 evaluated the performance of a mini Cu hollow cathode emission source for the analysis of Li, Na, K and Ca in microsamples (5.4

nL per aliquot). The aliquot were analysed as solution residues. Calibration graphs were rectilinear for up to 25 pg for each element, and the detection limits were 0.88, 0.72, 0.38 and 0.70 pg for Li, Na, K and Ca respectively. The technique was concluded to be adequate for analysis of nl samples of physiological fluid. Chen and Williams (1990) characterised a HCD device for the determination of $\leq$ 1 ng of P, Cl and Se in volume-limited physiological fluids. Better sensitivities were obtained by using a small sample volume (i.e., 0.85 nL as opposed to 50 nL) which was pipetted into the hollow cathode and dried in a separate chamber before inserting into the water-cooled HCD device. Using an Ar HCD, detection limits of 14 and 30 pg were obtained for P and Cl respectively, by integration of transient signal. However, no sub ng calibration can be achieved for Se.

Caroli *et al.* (1987) devised a new version of the microwave (MW)-boosted hollow cathode discharge which gives considerable improvement to the discharge. The performace of this lamp has been tested on Al, C (graphite), Cu, Fe, Mo and Ni cathodes; Cd and Pb solution dry residues on steel cathodes. In all instances significant increase in intensity of the emitted spectra, together with a noticeable diminution of background were observed; signal-to-background ratios of two orders of magnitude higher than those obtainable by conventional hollow cathode were achieved. An additional advantage of this lamp is its high stability of operation. Senofonte *et al.* (1991) used a microwave(MW)-boosted HCD for multi-element analysis (Ag, Al, C (graphite), Cu, Fe and Ni) of metal alloys as well as aqueous samples. Their results shows that the overall mass loss from MW-coupled HCD is less than in the normal operational mode of a HCD, whereas emission output increases considerably. Caroli *et al.* (1993) conducted comparative

studies on the analytical performance of the HCD and MW-HCD on the analysis of non-conducting materials (sediments and dry residues of solutions). The following elements were analysed: Al, As, P, Pb, S, Sb, Si, Sn and Ti. The MW boosted HCD source was found to enhance the spectral emission compared to that of the conventional HCD source as demonstrated by the slope of the calibration plots. Detection limits of powder sediments were not reported; detection limits of 10-100 ppb has been reported for dry residues of solutions using both the HCD and MW-HCD.

Obstructed Cathode Glow Discharge

In the Grimm (1968) or obstructed cathode glow discharges with flat cathodes, the discharge is restricted to a defined sputtering area on the sample surface. This is achieved by keeping the distance between the anode tube on one side and the cathode block which is the sample on the other side below the mean pathway of the free electron, i.e by extending the anode into the cathode dark space. The analyte is atomized by cathodic sputtering and is excited in the negative glow of the discharge mainly by electron impact. The emitted radiation is measured by end-on observation. The sample is located outside of the source for easy access and sample interchange. The typical operating conditions for a planar cathode glow discharge (Grimm source) source are 500-1000 V, 10-100 mA and 1-5 Torr.

This configuration is particularly adaptable to the analysis of metal sheets, disks, or any flat conducting sample that can be brought up to the source opening. Powder samples are pressed into the form of disk before they can be

analysed by GDAES. Nonconducting powder are mixed with powder conducting material such as Ag, Cu or graphite and compacted into disks.

Grimm (1968) introduced the glow discharge source for optical emission spectra analysis. Metal samples in the form of smooth plates are atomized in an Ar atmosphere. Detection limits for Si, Fe, Mg, Cr, Mo, Al and Pb were found to be at ppm range (2 ppm for Be to 100 ppm for Pb).

The analytical applications of the Grimm glow discharge lamp had been investigated thoroughly by Dogan *et al.* (1971;1972), El Alfy *et al.*(1973) and Boumans (1972) almost immeadiately after Grimm introduced his GD source .

Dogan *et al.* (1971) studied the electrical and spectral behaviour and analytical conditions of the Grimm glow discharge source for spectrochemical analysis of conducting and non-conducting samples. The followings are the conclusions of this study: (i) Stable electrical behaviour of the discharge is due to the voltage-current parameters which depends on the type of discharge gas and its pressure as well as on the composition of the sample. (ii) The rate of erosion by cathodic sputtering differs with samples of different composition and structure and depends upon the electrical parameters and the type of discharge gas and its pressure. (iii) The spectral nature of the discharge is due to the fact that no thermal equilibrium (i.e the discharge is non-LTE, see pp.21) exist between atoms, ions, and electrons in the source. The higher the ionization energy of the discharge gas, the stronger are the ion line intensities of the sample.

Dogan *et al.* (1972) studied the analytical application of the Grimm discharge source for the quantitative analysis of non-conductive samples (ground and mixed together with a current conducting materials, eg. Cu powder, and

formed into pellets). The precision of the analyses was found to be high if a suitable technique of measurement is used. Calibration curves are linear over a wide range of concentration (calibration curves were plotted in the range of an order of magnitude). Matrix and interelement effects were found to be small and in many cases not detectable. Therefore only a few standard samples or even one is needed in order to calibrate an analytical procedure. Spectral apparatus with high resolution was recommended due to the narrow analytical lines width in order to make full use of the power of detection. Detection limits ranging from 4.0×10^{-5} % for Cu to 1.5×10^{-3} % for Zn (using a medium quartz spectrograph) and 1.5×10^{-6} % for Cu to 3.6×10^{-5} % for Zn (3.4 m grating spectrograph) were determined for the analysis of Al (discharge conditions: carrier gas - Ar, current = 100mA, voltage 900V, preburn period = 45s, exposure time = 6.5s). This detection limits are comparable to those obtained with spark and interrupted ac arc. The disadvantages of the light source are the rather low intensity and the restricted burning (sputtering) time.

El Alfy *et al.* (1973a) used the Grimm GD source for quantitative analysis of electrically conductive and non-conductive samples. They described a universal method for the determination of main constituents in electrically nonconducting powder samples. Universal tehniques refer to those which enable "semiquantitative" estimates of concentrations with an accuracy characterized by a factor 1.3...2 in a great variety of substance after a single calibration. They concluded that high precision analyses could be achieved. They demonstrated that if the grain size of the powder sample is sufficiently fine (less than 50 μm), analytical performance are not affected by differences in the physical and chemical

properties of the conducting matrix and the sample. Therefore, calibration can be achieved by a single synthetic master-standard (in their case, the single master standard used was calcium carbonate and oxide).

Boumans (1972) measured the sputtering rates of metals and alloys in a Grimm glow discharge source and found a linear relationship between the mass sputtering rate per current strength and the operating voltage for these samples. For the analysis of trace and minor elements in precious metals like gold and silver using glow discharge emission source, satisfactory precision (better than 5% within the analytical range) and detection limits in the range of ppm levels were reported (Jäger, 1972; Ferreira and Butler, 1978).

Bubert *et al.* (1979) used a linear photodiode array (PDA) in conjunction with a Grimm-GD source to determine Al, C, Mg, and Si in powdered limestone. Calibration curves of these elements were reported to be linear over 2 order of magnitudes. Detection limits of a few tens of ppm were also reported. Bubert and Hagenah (1981) determined detection limits of Li, Na, K, Rb, Ba, Cs, La and Tl in electrically nonconductive powder rock sample. In this study and the earlier one, samples were mixed with Cu powder as the conducting matrix and compacted into a 25 mm diameter disk with a thickness of 2 mm. These elements have strong atomic lines in the wavelength range of 500-1000 nm when excited with GD emission source and the emission of these lines were detected by a silicon photodiode array. Linearity of the calibration curves were reported to be good within 4 to 5 order of magnitude (10^{-5} % to 10^{-1} %). Detection limits in the range of sub-ppm to ppm levels were reported (0.49 ppm for Li to 133 ppm for Tl).

In their application of the Grimm GD source for the analysis of geological and related materials, Brenner *et al.* (1987) demonstrated that material transported from the surface of the pellet into the discharge zone is predominantly due to the sputtering process and the thermal effect which result in selective atomization is found to be absent. As a result of this, analytes entering the discharge zone is representative of the bulk material. Despite the variable textural, mineralogical and chemical compositions of the calibrating standards, the linearity of the calibration curves are satisfactory, which imply small matrix effects due to these differences. Linearity of the calibration curves were reported to be good for 2 orders of magnitude (0.2 %-6.0 %). The self absorption effect in this source is also found to be small, hence linearity is preserved between the intensity ratio and the certified concentration of the standard geological materials which cover a wide concentration range. The authors concluded that GDAES is a viable technique for the direct simultaneous or sequential multielement analysis of a wide range of solid geological and other nonconducting material.

Mai and Scholze (1986, 1987) investigated atomic transport phenomena in a glow discharge source during the analysis of compacted powder. They concluded that atomic transport due to solid state reactions and the sputter/redeposition cycle had resulted in the steady state formation and the reduction of matrix effects during GD excitation.

Ehrlich *et al.*(1991) extending the work of Mai and Scholze, concluded that the atomic transport process during GD excitation of finely dispersed briquetted analytical subtances (grain size less than 60 μm) blended with an excess of fine copper powder reduced the influence of the binding energy of the

analyte elements and of other matrix effects to such a degree that semiquantitaitve results can be obtained from a single set of calibration standards by GDAES.

Wagatsuma and Hirokawa (1985) investigated emission lines and the relative intensities of Cu, Ag, Sn. Al and Zn in the wavelength range of 200 to 600 nm excited in a GD emission source using argon, neon and nitrogen separately as the discharge gas. The emission spectrum pattern of these metallic element strongly depended on the kind of discharge gas rather than the discharge conditions such as the gas pressure and the discharge voltage. Especially, the emission from singly ionized species are drastically affected by changing the discharge gas when other conditions are kept constant. These observations suggest that the energy levels and their excitation energies of each foreign gas play significant roles in determining the ionization and excitation of the analyte atoms.

Broekaert *et al.* (1990) examined Fourier transformed (FT) processing of the emission signal from a Grimm-type GD source, which they concluded, enable for flexible multielement analysis with high resolution, (line width in pm range). Detection limit approaching those obtained with wavelength-dispersive spectrometers was reported, eg. the limit of detection of Mo for the analysis steel was reported to be 30 ppm using GDAES source coupled to a FTS.

Atomic-emission spectroscopy using a jet-assisted GD source AES modelled on the commercial Atomsource (Analyte Corp., Grant Pass, OR, USA) was investigated by Banks and Blades (1989). The source differs from the Atomsource in that end-on detection was used instead of side-on detection. The anode-cathode voltage, current and power were reported to be relatively independent of jet-gas flow rate. Although application of the jets reduces re-

deposition which resulted in enhanced sample atomization (sample loss rate increased by a factor of 3 times over the situation with no flow) at fixed pressure and power, as did an increase in power, emission intensities of Cu I 324.75 nm and Cu II 224.70 nm were not enhanced. In fact, some lines with high absorption coefficients were reduced in intensity. This resulted from the directional entrainment of sputtered atoms by the jets along the optical path, which increase self absorption.

A number of workers have reported the use of dc-boosted discharge to enhance the sensitivity of GDAES (Lowe, 1976; Gough and Sullivan 1978; Lomdahl *et al.* 1983).

A boosted glow discharge emission source, based on the source described by Grimm (1968) which uses a plane cathode was described by Lowe (1976). This GD source was constructed of glass with the inclusion of a d.c. secondary or boosted discharge of high current density. The function of the secondary discharge (where majority of the excitation of metal atoms now takes place) is to increase the excitation of sample atoms sputtered. Analysis of metallic alloy (Al-base alloy) using this source demonstrated an increase in intensity of the spectral lines of the sputtered atoms (~ 12 times) without an increase of rare-gas lines leading to less complex spectra. An improvement in signal-to-noise ratios is therefore observed due to the increase of the metal lines intensity. Gough and Sullivan (1978) used a boosted glow discharge source similar to that described by Lowe but constructed from metal in order to permit efficient cooling in conjunction with a polychromator to determine simutaneously a number of metals of various concentrations in different alloys (matrices). Enhancement in resonance lines is

sufficiently high so that detection of metals in these alloys at concentrations of a few ppm was possible. The precision of the measurements of major, minor and often trace constituents in alloys with relative standard deviation of approximately 1% can be achieved. The same source was applied to the analysis of nonconducting material (Ni, Cu and Fe oxides) by Lomdahl *et al.* (1983).They investigated the factors influencing the determination of these metal oxides. The oxides were mixed and pressed with a conducting binder (Fe, Cu and Ni) to pellet. They concluded that good precision (1 %-2 %) may be achieved if the powders are properly mixed and adequately outgassed. They recommended that binder element chosen should give minimal spectral interference. Detection limits of a few ppm for the metal oxides (2 ppm for NiO and 1.5 ppm for CuO) were reported in Cu and Ni binders.

Radio Frequency Glow Discharge Atomic Emission Spectrometry (rf-GDAES)

One of the more recent areas of GD development is the coupling of radio frequency(rf)-powered GD sources with various analytical atomic spectrometric techniques. The direct solids analysis by the dc-powered GD spectrometry have been excellently complemented by the radio-frequency discharges. Indeed, the use of dc discharges is limited to conducting materials, whereas the rf discharges are applicable to electrically nonconducting samples. Hence matrix modification steps are no longer necessary for analysis by rf-GD techniques. The primary distinct advantage of rf-GD over traditional spectrochemical sources therefore lies in its inherent capability for the direct solids analysis of both conductive and nonconductive samples. Beside this, rf-powered GD source has been shown to have higher excitation temperatures (≈6000 vs.

≈2500 K) and higher electron temperatures (≈1.8 vs. ≈0.6 eV) than the dc versions (Winchester *et al.*, 1991). These characteristics lead one to believe that the rf discharge should be more efficient for excitation of high excitation-energy lines (Montaser, 1992). The operational principles, various source designs and the instrumentation involved in the rf-GDS have been described by Marcus *et al.* (1994) recently in a number of papers.

The atomization/excitation/ionization processes in rf-GD are maintained through two electrodes (one which is analytical sample) immersed in an inert gas such as argon. Unlike dc discharges in which both electrodes need to be electrically conducting to sustain the required flow of current, one of the electrodes can be an electrical insulator.

Winchester and Marcus (1990) used a 13.56 MHz rf-GD source for analysis of nonconductive solid materials by AES which were sucessfully atomized to some extent and ionized in the rf-GD without the need to mix them with graphite powder. Spectra (obtained from side-on view) of brass and glass standard reference materials were both rich in atomic lines, suggesting a good atomization efficiency. Plasma stability of non-conductive samples are comparable to those with conductive samples. The Ar pressure and the applied rf power was found to affect the emission intensity. Extending their earlier work, Winchester and Marcus (1991) incorporate two optical windows for comparison of emission intensities viewed end- or side-on on for the analysis of ceramic sample. Signal-to-noise ratios obtained for both optical geometries were found to be similar. Emission intensities measured with the end-on geometry were 2-5 times higher than the side-on geometry owing to the more complete viewing of the energetic regions; hence this

geometry may be considered to be analytically more advantageous. Conditions of higher power (60W) and pressure (6-10 Torr) were needed to provide attractive emission intensities of the sputtered species. Pan and King (1993) employed radio frequency (rf) powered glow discharge pulsed at 50Hz as analytical AES source for the determination of trace elements in coal fly ash (Ca, Cu, Co and Cr) and graphite samples (Fe, Cr and V). Detection limits in ppm range were reported for trace elements in coal fly ash (3 ppm for Co to 62 ppm for Ca) and graphite (13 ppm for Cr to 35 ppm for V). The ability to operate the rf glow discharge with greater instantaneous powers in the pulsed mode than in the steady-state mode results in enhancement of analytical signal (by 4 times) was demonstrated. This observation had also earlier been reported by Winchester and Marcus (1992) when studying the emission characteristics of a pulsed, rf-GD atomic emision device. The analytical figures of merits for trace elements in precious metal alloys have been evaluated using rf-GDAES by Harville and Marcus (1995). Calibration plots with linearity over 2-3 orders of magnitude were reported with a general improvement in linearity by ratioing the signal to an internal standard which also improved analytical precision. Similarities in sputtering rates which allow for multimatrix calibration, emphasizing on the fact that matrix effects within the glow discharge was neglible.

1.7.2 Glow Discharge Atomic Absorption Spectrometry

The sputtered atoms in a glow discharge are mostly present as atoms in their ground state. The glow discharge source is therefore a suitable atom reservoir, making it potentially useful for atomic absorption spectrometry (AAS).

The use of cathodic sputtering as a means of atomising samples for atomic absorption spectroscopy was proposed by Russell and Walsh (1959), soon after the introduction of atomic absorption technique. The first sputtering atomiser that was reported required the sample to be in the form of a hollow cathode and to be mounted inside the sputtering chamber (Gatehouse and Walsh,1960). An improved sputtering atomiser described by Gough *et al.* (1973) which allowed solid samples with a flat face to be mounted onto the outside of a glass chamber against an insulating disk (called a discharge arrester) and O-ring. The system utilized a flowing stream of argon to help remove gaseous impurities from within the chamber, but was not satisfactory for the analysis of readily oxidized metal such as aluminium or zinc. A modification to the design of the earlier sputtering atomiser was reported by Gough (1976a) where the argon was introduced as closely as possible to the sample surface. In this atomiser (Figure 1.10(a)) the gas is admitted into the chamber through a narrow (0.1 mm) annular gap located just below the cathode surface (Figure 1.10(b)). The pressure developed behind the narrow gap forces the gas to enter the sputtering chamber at high speed. This arrangement has the two advantages: (i) the fast gas flow entrains sputtered atoms, greatly reducing lateral and back diffusion, and sweeps them into the light path resulting in an increased absorption sensitivity of typically an order of magnitude; (ii) The rapid flow of gas at the cathode surface sweeps away gaseous impurities and thus allows metals such as aluminium to be analyzed without difficulty. Gough uses this source for the analysis of metals and alloys by AAS. Antimony, Be, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Ag, Si, Ti, V and Zn were determined in alloys of Fe, Al, Cu and Zn; each determination took 2-10 minutes depending on the type of

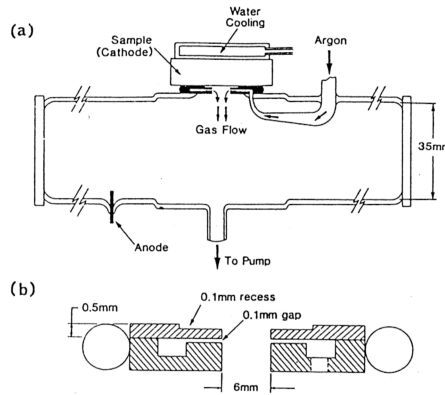


Figure 1.10 (a) Schematic diagram of Gough's glass sputtering atomizer.
(b) Schematic diagram of the hollow silica arrester used with this atomizer for admitting gas into the atomizing chamber. The gap and recess dimensions are also given in this diagram.
(From Gough, 1976)

alloy. Precison was good (1 %-3 %) and detection limits ranges from 3 to 400 ppm were reported.

McDonald (1977) used the atomiser developed by Gough and adopting the use of internal standards for the AAS analysis of Fe, Cr, Ni and Cu in solid alloys (steel, Al and Brass) and powdered metallic and nonmetallic samples. Powdered samples were compacted into the form of disk. The ratio of the analyte absorbance to the absorbance of an internal standard element in the sample was compared with the corresponding ratio in a standard reference material. This allowed accurate determinations to be made even when the sputtering rate of the sample was quite different from that of the reference sample. Precisions for the analysis of the elements in solid alloys and compacted powder sample was reported to be equal or better than ± 8%.

Trace analysis of aqueous solution residues using GDAAS have been reported by Bruhn and Harrison (1978). The analysis of Ca, Mg, Zn, Au, Ni , and Sn in solution residues shows detection limits ranging to a few ng with precisions of 3-8 %. Headrick *et al.* (1994) noted severe matrix interference in the use of the Atomsource, a commercial cathodic sputtering atomiser for the analysis of solution residues by AAS. Interference can result from the presence of matrix (such as NaCl) which readily arcs and prevent the formation of a stable glow discharge, thus producing no significant cathodic sputtering. Interferences can also occur as a result of chemical reactions between the matrix and cathode material, and changes in the viscosity and the surface tension of the sample solution on the cathode surface. Peak- area absorbance has been shown to be much less subject to matrix interferences than peak height absorbance. Graphite cathodes have been

found to give better recoveries than copper cathodes for acidic matrices. The use of peak area absorbance instead of peak height absorbance and the judicious choice of cathode surface has been shown to remove some of these interferences.

Recently, the use of a rf-GD device as an atomization source for atomic absorption spectrophotometry was introduced by Absalan *et al.* (1994). The spatial distribution of Cu atoms sputtered from an oxygen-free hard copper sample has been investigated. Inhomogeinity of the glow discharge medium was noted; most of the analyte atoms (in this case Cu) are localized infront of the sampling orifice. It was found that independent of flow rate controlling and pressure of sputtering gas was critical for controlling the spatial distribution of sputtered atoms. The authors also concluded that rf GD source was able to sustain a plasma stable enough for sequential AAS and depth profiling of metal samples.

The commercial cathodic sputtering atomiser, the Atomsource (from Analyte Corporation, Grant Pass, Oregon, USA) designed for AAS was introduced in 1987 for direct analysis of solid conducting samples. The design of this atomiser is the same as the one introduced by Gough (1976) except that its body is metallic while the body of Gough's atomiser is made of glass. It uses the principle of direct supported gas flow introduced by Gough. The atomisation by sputtering is a nonthermal process, hence the Atomsource was used to determine elements that form refractory oxides in flame and furnace atomisers (eg., B, Ce, La, Nb, Si, Ti, W amd Zr) ; sensitivities comparable to those obtained for non-refractory elements were reported. For solid samples, atomic absorption detection limits are in the low ppm range (Bernhard, 1987; Ohls, 1987 & 1990). Kim and Piepmeier (1988) have reported detailed studies of the sample loss rates and

discharge conditions in the Atomsource and also in a simple, single-jet atomiser. The authors have shown that the use of six gas jets (as in the Atomsource) significantly increases the rate of sputtering over that provided by either a static system (i.e. with no gas flow) or the use of single jet. Surface sputtering was also reported to be more uniform when gas jets were used. They concluded that the gas-jet enhanced sputtering should decrease preferential sputtering and matrix effects and present a highly representative fraction of the sample to the spetrometer for analysis.

Winchester and Marcus (1988) reported the analysis of nonconducting (oxide) powder samples using the Atomsource. The oxide powder was mixed with a copper host matrix. They reported sample-to sample precisions on the order of 3 to 4 % for iron in a geological sample (NBS 69A bauxite). The ability to generate analytical curves is demonstrated for the analysis of Fe by mixing Fe (III) and Al (III) oxides in the copper matrix (Fe concentration, 0.15-0.76 %). The analysis of Fe in the geological sample with an analytical accuracy in the order of 8% was demonstrated using the calibration curve obtained from standards of like matrix to the sample. The ability to perform analyses on samples of these types suggest its applicability to such matrices as ceramics, glasses and refractory-based catalyst by the authors. Gough *et al.* (1989) studied factors influencing absorption sensitivity and reproducibility for several atomisers, including the Atomsource and an earlier system (Gough, 1976). They reported enhancement in sensitivity (by a factor of 3) of the Atomsource over that of the earlier system developed by Gough, for given sputtering conditions. This is mainly

a result from the increased absorption path length in the Atomsource due to efficient sweeping of sputtered atoms along the light path.

The transient and pulse modes of atomization by cathodic sputtering of aqueous solution residues for the ultra trace analysis of 14 elements was incorporated with the Atomsource recently (C.L. Chakrabarti *et al.*,1990). These modes were introduced to overcome the kinetic limitations of the atomization process in the steady state mode which resulted in poor sensitivity by rapid production of analyte atoms to produce greater transient concentration of atoms in the analysis volume than the steady state mode. Detection limits comparable to those for GFAAS were reported (7.0 pg for Al to 1600pg for Pb). Linearity of the calibration curves extended over 10^3 ng were demonstrated for Mg. Sensitivities for these elements within an order of magnitude of the GFAAS were also reported. Matrix interference appear to depend on the conductivity of the matrix. Peak area absorbance was found to be not affected by the matrix interference whereas peak height absorbance is. Alkali and alkali earth metal chlorides demonstrated severe interference with other elements for both peak area and peak height absorbance. The used of peak area absorbance rather than peak height has been found to eliminate interferences when the matrix is conducting. The use of rf-discharge for the analysis of non-conducting solution residues and powder sample has been suggested to overcome the martix interference.

Pan and King (1993) used the transient mode atomization GDAAS for the direct determination of trace elements (B, V, Fe and Cr) in graphite matrices. The method of standard addition was used to determine the impurity levels of the standard graphite matrix. Graphite powder mixed with different

standard solutions separately were dried, homogenized and compacted into disk of 5 mm in diameter. Linear analytical calibration curves were obtained for the 4 elements and detection limits in tens of ppb for graphite matrices (19 ppb for Cr to 64 ppb for B) were reported.

Chakrabarti *et al.*, (1991) and Hutton *et al.* (1991) evaluated the performance of a new laboratory constructed cathodic sputtering atomiser with gas jets directed at the cathode surface (this feature is similar to the commercial atomiser, Atomsource). The evaluation was conducted on solution samples of metal elements (Ag, Au, Co, Fe, Mg and Ni) dried on metal cathodes and bulk brass and steel sample (Cu, Ni and Cr). The new atomiser allows for the independent control of argon flow rate and pressure while the Atomsource does not. This feature was observed to afford an increase in the ratio of the rate constants for (i) conversion of the analyte which has not entered the analysis volume into analyte atom that absorbs radiation and (ii) conversion of the latter species into analyte atom that is removed from the analysis volume. The pressure and power have been found to affect sputtering rate (atomization efficiency) whereas argon flow rate seems to have significant effect on the rate of supply of analyte atoms to the analysis volume (transport efficiency). Ground state population within the analytical volume was found to be dependent on the sputtering and transport efficiency. For solution residue samples, peak height sensitivity increased by a factor of ≤ 5 over that of the Atomsource and peak area sensitivity is improved by 1 to 2 orders of magnitude. These sensitivity were reported to be equal or better than the GFAAS. Detection limits based on peak area range from 0.21 pg for Mg to 34 pg for Ag, which is 2-3 order of magnitude

lower than the Atomsource. Detection limits for the bulk solid samples were not reported.

The typical operating conditions for GDAAS (Gough, 1976; McDonald, 1977; Tong and Harrison, 1984; Gough *et al.*, 1989) are 4-10 Torr, 60-200 mA and 300-800 V. Detection limits of trace metal elements for bulk metal solid samples are generally in the low part-per-million (Gough, 1976,).

Sample preparation in GDAAS (Gough, 1976; Pan and King, 1993; Chakrabarti *et al.*, 1988) is very much the same as for other GD techniques. Metal or alloy disks or compacted conducting samples are most often used. Solution samples have been examined by deposition onto graphite, aluminium, or copper cathodes followed by drying. Nonconductors such as oxide materials must be mixed with conducting powder, eg. copper powder and pelleted by using pressure of 10^4 psi magnitude (McDonald, 1977; Winchester and Marcus, 1988; Pan and King, 1993). It was observed that different behaviours of sputtering may be observed for the same nonconductive sample materials when they are mixed with various metal powders for pelleting (Ohls, 1987; Winchester and Marcus, 1988). Quantitative analysis is typically performed with a calibration curve prepared from standard reference materials, a process requiring considerably more time than the preparation of a corresponding solution based curve. Conversely, much time is saved in the direct analysis of solids and also the inert atmosphere of a GD cell reduces the chemical interferences sometimes found in flame atomisers.

1.8 Reactive Species in the Glow Discharge and their Effects on the Analytes and Discharge Gas Species

Various reactive species are known to be present in the glow discharge plasma of compacted solids. These include primarily the O, H and N species. These reactive species could be derived from the discharge gas supply, trapped in the sample during sample compacting or being the principal constituents in the sample. The presence of trace amount of hydrocarbons in the discharge chamber is also possible since vacuum pump are used in GD system. Reactive species have been established as "harmful" to the glow discharge as an analytical tool because they interact with the energetic discharge gas species and also the analytes in the GD plasma.

The negative glow of GD is the region in which species such as Ar^+, metastable argon, Ar^m, energetic electrons, ground state analytes, M, ions of analytes, M^+, and excited atomic species of analytes, M*, are found. The interactions of these species play an important role in affecting the population of the different kinds of analyte species in the plasma. The density distribution of the analyte species will determine the analytical signal quantitatively. However, the interactions of these species are often complicated by the presence of reactive species in the plasma. The complication sets in when the reactive species begin to negatively affects the interaction between Ar^m and ground state, ions and excited species of the analyte in the negative glow by (i) energetically quenching the excited analytes species and Ar^m and (ii) forming compounds with the analytes thus reducing the atomic species in the plasma, eg. they form oxides, hydrides, nitrides etc. with the analytes, thus lowering analytes free atomic species and

therefore the various atomic/ionicanalytical signal.. These processes (interactions) affect the density distribution of analytes atoms and the Ar metastable species negatively.

The effects of atmospheric residual and water vapors, which effectively quench the important metastable levels of the discharge gas atoms and inhibit the cathodic sputtering process are well documented in recent papers by Larkins (1991) and Ohodrodnik *et al.* (1993). The sputtering of oxide samples such as glasses and ceramics most certainly introduces large amount of oxygen into the plasma. Glasses and ceramics, which tend to be somewhat porous, also act as sources of water vapour that is liberated from the matrix through the sputtering process.

Lindinger (1973) proposed a variety of possible reactions involving Ar and H_20 in a study using a steady-state hollow cathode discharge with 0.55% H_20 in Argon. From these proposed reactions he deduced that argon ions responsible for the sputtering processes could be consumed by reactions with water vapour and its residue. The consequence of these reactions is the reduced sputtering of analyte species by the energetic argon ions.

The presence of water vapor in the argon sputtering gas at levels greater than 10 ppm was reported to have a deleterious effect on the sputtering efficiency and reproducibility by Gough *et al.* (1989). They suggested that the use of "dry" argon that was free from water (i.e., at levels less than 10 ppm) will enable the best results to be obtained.

Larkin (1991) also investigated the effect of water vapour on atom production by glow discharge sputtering. He reported the reduction of free atoms

measured by GDAAS in the presence of water vapour. He suggested that the lowering in the absorbance signal of free atom was due both to interference with the sputtering process, which resulted in lower sample erosion rates and to some process which occured after the atoms were sputtered, probably gas phase reaction between sputtered metal atoms and water molecule or its fragments. Hence it is necessary to ensure that the contamination by water vapour is kept to a minimum during the design and operation of sputtering systems. The effect of water vapour in reducing the absorbance is worsen at low currents.

Several conventional measures have been taken to minimize water vapour and organics contaminations. These measures include the use of ultra-pure argon; the installation of molecular sieve in the vaccum line to remove organic vapour coming from the backdiffusion of vacuum pump; and the keeping of the discharge chamber from any vaccum leak. However these preventive steps taken to avoid contamination during the operation of the glow discharge may be inadequate since reactive could also be present in the sample itself (especially trapped trace amount of water vapour and air during the compaction of compacted disk). A number of fundamental studies have been reported to eliminate the interfering reactive species by physical processes and the modification of the "plasma solution".

Optical and mass spectrometric diagnostics were applied in a study of chemical reactivity of the plasma impurity species in an r.f. glow discharge source by Ohorodnik *et al.* (1993). Cryogenic cooling was incorporated within the GD source to investigate potential interactions. Significant increases were observed in the sputtering gas (in this case Ar) and cathode matrix (Cu, Fe and Ta) ion

signals as well as the ground- and excited-state populations of the cathode matrix species with cryogenic cooling. The enhancement of the analyte signal however was also found to be dependent on the sample matrix. For example a smaller improvement was observed in oxygen-rich samples such as geological samples. The atomic oxygen sputtered into the plasma from these samples was "inacessable" to the cryocooling process and was removed primarily by getter action.

In the analysis of non-conducting samples such as rare earth oxides, geological samples, and glasses for dc GD discharge, the samples are required to be mixed with a conducting powder which serve as the host matrix. In principle, any metal can be used for this purpose, however if chosen properly, the matrix metal not only provides the conducting medium, but can also influence favorably the plasma chemistry for analytical purposes. An important factor that can influence plasma chemistry is the presence of residual water in the discharge. A substantial amount of water is absorbed on the granular surfaces of metal oxides and released into the plasma during sputtering. A plasma containing water is oxygen-rich, which promotes the oxidization of analyte atoms. This will lower atomic ion or emission signals. For compacted samples, a practical way to minimize water vapor in the plasma is desired. One way of reducing the oxygen sputtered into the plasma is by using getter reagents as the conducting host matrix. Getter reagents are highly reducing metals that readily react with species containing O_2, N_2, C and H_2. Mei and Harrison (1991) evaluated five metals Ti, Ta, W, C and Ag with varying gettering abilities in their study for removing gaseous interferences in the discharge and enhancing atomic population of the

analyte. Among the five elements, Ti and Ta present effective getter action due to their high M-O bonding strengths.

Tong and Harrison (1993) investigated suitable matrix materials and optimum discharge conditions for GDMS analysis of non-conducting materials. The effect of metal oxide (M-O) bond strength on oxide ion formation was also demonstrated. They concluded that the GD plasma was able to produce primarily atomic mass spectra, but oxide ions contribution could create problems for elements of high oxide bond strength hence getters were suggested as matrix materials to modify the plasma chemistry. The authors sought the use of matrix material that could act as getter reagent since trace impurity gases (eg. O_2, N_2 and H_2O) can cause significant spectral interference by forming oxide, hydride or hydroxide ions of many elements which may impinge on other elemental ions of the same nominal mass. Getter reagents can reactively remove these impurities from the plasma, while still meeting other desired characteristics for GDMS. The conducting matrices studied by them include Cu, Ag, C, Fe , Al and Ta. Based on the mass spectral simplicity and reduction of oxide ions, Ta was found to be the best conducting matrix when compared to graphite, Cu, Ag, Fe and Al.

Teng *et al.* (1995) examined the influence of oxygen content, conducting host matrix (Ag, Cu, Ta, Ti and Zn were used as the host matrix) and soil composition on the quantitative determination of trace elements in soils by GDMS. They found that sample cathodes with oxygen contents above 20% yielded glow discharge with such instability that meaningful measurements were precluded. Reliable determinations required dilution of the nonconducting sample material with a conducting host matrix to yield a cathode of 5% or less oxygen

content. The type of conducting material used as the matrix has been found to affect the relative sensitivity factors (RSF). RSF is defined as the ratio value of the real concentration to measured concentration. In selection of the matrix material, the authors suggested the following criteria crucial for consideration: purity, sputtering yield, hardness, melting point and possible spectral intereferences with elements of interest. These points for consideration are applicable also to GDAES. A number of reports have claimed that Cu was the most suitable matrix material since it yielded the best considerations of high sputter yield, cathode sample durability, high matrix purity, economic availability and atomic weight (eg. McDonald, 1977; Brenner, 1987; Winchester and Marcus, 1988).

1.9 Limitations in Current GDAES Techniques for Direct Solids Analysis

The GDAES technique with its various configurations have been proven to be a suitable and potential technique in complementing other AES techniques such as the arc and spark AES techniques for direct solid analysis. However, there are still limitations in these techniques which have to be overcome and further enhancement in its analytical performance are necessary.

The hollow cathode discharge technique has been demonstrated capable of achieving detection limits at ppb and sub ppb levels for solution residues analysis. However, very few studies have been reported in the application of this for direct solids analysis and they have not been very sucessful in achieving ppb and sub ppb detection limits level.

Numerous studies on the analysis of major, minor and trace elements in conducting and nonducting powder samples using the Grimm and

planar glow discharge source have been reported and detection limit at ~ 0.1 ppm have been achieved. The analysis of nonconducting powder samples require the mixing with a high purity conducting binder and then compacted to form conducting pellets. Most often copper powder and graphite have been used, and in a few cases use of silver powder have been reported. The sucessful application of this approach depends very much on the characteristics of the conducting matrix materials. The use of Cu and graphite powder as compacted matrix materials has been reported recently to give rise to various unfavourable conditions to the interactions in the GD plasma. These have been attributed to persistent water and other reactive species generated from the compacted samples and the source chamber (Tong and Harrison, 1993; Ratliff and Harrison, 1994). Other drawbacks dependent on choice of the conducting matrix used for compacting include (i) dilution of the nonconducting samples and (ii) spectral interference from atomic emission of atomic species of the compacting matrix materials.

A few recent studies have been focused on the investigation of the effects due to the interactions between the sputtered analytes and inherent reactive species (O, OH, H etc.) generated together from compacted samples in the GD plasma. These interactions have been found to be negatively affecting the ionic, atomic absorption and emission signals (Gough, 1976; Gough *et al.*, 1989; Larkins, 1991; Mei and Harrison, 1991; Tong and Harrison, 1993; Ohodronik *et al.*,1993; Ratliff and Harrison, 1994) which limit the analytical performance of these sources in term of precision, sensitivity and detection limits. A number of these studies on GDMS have been looking into the use of alternative compacting matrices in order

to reduce the matrix dependent factors which affect the analytical performance (Mei and Harrison, 1991; Tong and Harrison, 1993)

Very few studies have been reported on the improvement of the analytical performance of GDAES by considering the use of different conducting matrix materials and attempting to overcome the inherent problems relating to matrix effects for the analysis nonconducting powder samples. The matrix effects include those which affect the sputtering process of the analyte due to the difference in physical and chemical properties of the host matrix and sample, and also effects due the production of reactive species such as OH, O and H in the GD plasma matrix which can affect excitation and ionization processes. It is therefore the intention of the present study to investigate the physico-chemical matrix modification method to (i) modify the "physical nature" of the compacted solid itself so as to improve the sputtering process, and (ii) to alter the chemical "nature" and processes in the GD plasma by reducing or eliminating potential reactive species, for improving the analytical performance of the GDAES technique for nonconducting powder sample analysis.